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AB INITIO CHARACTERIZATION OF C_4^-, C_4H, AND C_4H^-

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ABSTRACT

Using state-of-the-art theoretical methods, we investigate the stable isomers of C_4^-, C_4H and C_4H^-. Three of them are relevant for astrophysics and astrochemistry. These computations are performed using highly correlated ab initio methods and the aug-cc-pVXZ (X = T,Q) basis sets. In addition to the linear isomers, we predict the existence of several cyclic and branched forms for these molecules. For all the molecular species of interest here, sets of spectroscopic parameters are determined with perturbation theory, which compare quite well with experiment. For $l - C_4H^-(X^1\Sigma^+)$, the quartic force field is computed at the coupled cluster level of theory. This force field is derived from full nine-dimensional potential energy surface generated close to the equilibrium geometry of this anion. Finally, we treat the thermochemistry of the hydrogen attachment and the electron attachment reactions that may lead to the formation of the C_4H^- from either C_4^- or C_4H.

Key words: astrochemistry – ISM: molecules – molecular data – molecular processes

Online-only material: machine-readable table

1. INTRODUCTION

The recent detection of negative charged species in the interstellar and circumstellar media has instigated enthusiasm for the anions in the astrophysical community and laboratories dealing with astrophysical processes (McCarthy et al. 2006). Many of these detected species are new and entail study and characterization. How they are formed in the astrophysical sources is a question of major relevance (Herbst & Osamura 2008; Harada & Herbst 2008).

The presence of anions in astrophysical sources was first considered by Dalgarno and McCray, in 1973 (Dalgarno & Mc Cray 1973). In 1981, Herbst predicted anion formation in dense clouds from radicals of more than four atoms (Herbst 1981). However, the actual interest is recently coming from the discovery of C_6H^- by McCarthy et al. in 2006, using Fourier transform microwave and millimeter-wave spectrometers. This detection has been crucial and has generated the search of C_4H^- (Cernicharo et al. 2007; Agúndez et al. 2008; Sakai et al. 2008), C_6H^- (Kasai et al. 2007; Sakai et al. 2007), C_8H^- (Remijan et al. 2007; Kawaguchi et al. 2007; Brünken et al. 2007), C_3N^- (Thaddeus et al. 2008), and C_5N^- (Walsh et al. 2009) in astrophysical sources. C_4H^- has been observed in the envelopes of the carbon-rich star IRC+10216 and the protostar LI527.

It is commonly admitted that the structure of C_nH^- anions is very similar to that of the parent neutral radical. For $n = 4$, both C_4H and C_4H^- show linear geometries in their ground electronic states (McCarthy et al. 1995; Botschwina & Oswald 2008). C_4H was earlier detected (McCarthy et al. 1995; Botschwina & Oswald 2008) and experimentally characterized (Shen et al. 1990). The studies of C_4H^- are the newest. In 1998, Taylor et al. determined the electronic and the vibrational structure of the neutral C_4H and C_4D through the analysis of the photoelectron spectra of their anions. They deduced the adiabatic electron affinities of C_4H and C_4D to be 3.558 ± 0015 eV and 3.552 ± 0.015 eV, respectively. Moreover, several anionic electronic states were characterized by the group at Basel via the analysis of the electronic transitions of C_4H^-. These studies have been performed in gas phase using photodetachment spectroscopy in the vicinity of their electron detachment thresholds (Pino et al. 2002; Grutter et al. 1999). Their assignments lead to frequencies of 430 ± 5 cm^{-1} and 212 ± 5 cm^{-1} for the ν_6 and ν_7 large amplitude modes of the C_4H^- ground electronic state. Recently, in 2007, the rotational spectrum of C_4H^- has been recorded by Gupta et al. (2007), who provided spectroscopic constants for C_4H^- and C_4D^-. Amano has detected C_4H^- in electrical discharge in the submillimeter-wave region and reports rotational constants and transitions up to $J = 54$–53 (Amano 2008).

An important question treated in many papers, is how the C_nH^- species are produced in astrophysical environments. It is generally accepted that gas-phase processes are crucial. Hydrocarbon radicals C_nH may be the main precursors of the C_nH^- anions through electron attachment ($C_nH + e^- \rightarrow C_nH^-$) or association processes ($C_n^- + H \rightarrow C_nH^-$), whereas associative detachment processes ($C_n^- + H \rightarrow C_nH + e^-$) contributes to the generation of neutral C_nH. Recently, Herbst & Osamura (2008) and Harada & Herbst (2008) have included both processes in their OSU network for modeling the formation and decomposition reactions of carbon chains anions in interstellar and circumstellar media. More recent is the paper of Walsh et al. (2009) where carbon chain anions are explicitly considered in reaction models and for the determination of molecular abundances. Experimentally, Barckholtz et al. (2001) have treated the reactions of C_n^- and C_nH^- with hydrogen and molecular hydrogen. Interestingly, they found that C_n^- chains do not react with molecular hydrogen but extremely reactive with atomic hydrogen. They remarked also that reaction channels depend on the number of carbons: small carbon chains produce mainly neutral C_nH species, whereas large carbon chains produce either C_nH^- or C_nH. These authors proposed an explanation for these findings after density functional theory computations on the enthalpies of these reactions.

In the literature, nothing is said however about the C_4H^- formation by association processes and few information is available concerning its molecular properties. In the present paper, we start the characterization of C_4H^- by means of state-of-the-art single- and multireference ab initio approaches and extended

Table 1
Electronic Energies (in Hartrees, E), Relative Energies (in eV, E_r), and Structural Parameters (distances in Å; angles in degrees) of C_4^- Isomers

Isomers		(R)CCSD(T)	CASSCF[a]	RCCSD(T)[b]
		aug-cc-pVQZ	aug-cc-pVQZ	Spectroscopic Parameters
$l-C_4^-$	$X^2\Pi_g$	$R_0 = 1.2815$	$R_0 = 1.2730$	$B_e = 4944.9803$
($D_{\infty h}$)		$R_i = 1.3404$	$R_i = 1.3263$	2108 (σ_g), 1763 (σ_u), 965 (σ_g)
		$E = -151.973694$	$E = -151.491927$	514 (π_g), 255 (π_u)
		$E_r = 0.0$	$E_r = 0.0$	$\mu = 0.0$
$r-C_4^-$	X^2B_{2g}	$R = 1.4552$	$R = 1.4589$	$A_e = 38715.6458$, $B_e = 13339.4022$
(D_{2h})		$R_d = 1.4750$	$R_d = 1.4846$	$C_e = 9921.1045$
		$\theta = 59.7$	$\theta = 59.4$	1380 (a_g), 1276 (a_g), 984 (b_u)
		$E = -151.922616$	$E = -151.443535$	503 (a_g), 491 (a_u), 272 (b_u)
		$E_r = 1.39$	$E_r = 1.32$	$\mu = 0.0$
$d-C_4^-$	X^2B_1	$R_0 = 1.3061$	$R_0 = 1.2954$	$A_e = 46373.5566$, $B_e = 8740.6170$
(C_{2v})		$R = 1.4983$	$R = 1.5336$	$C_e = 7354.4330$
		$\theta = 153.3$	$\theta = 154.5$	1655 (a_1), 1411 (a_1), 777 (a_1)
		$E = -151.924472$	$E = -151.437356$	609 (b_2), 382 (b_1), 141 (b_2)
		$E_r = 1.34$	$E_r = 1.48$	$\mu = 0.9320$

Note. Equilibrium rotational constants (in MHz), harmonic frequencies (in cm^{-1}), and dipole moment (in Debyes).
[a] Active spaces have been defined containing 13 orbitals C_4^- and 14 orbitals C_4H and C_4H.
[b] $l-C_4^-$ frequencies and all the dipole moments were calculated at the CASSCF/aug-cc-pVTZ level. Dipole moment origins are the centers of mass.

basis sets. For the stable isomers of C_4H^-, we deduce a set of accurate spectroscopic properties of these species in their electronic ground, including equilibrium geometry, rotational, harmonic, and anharmonic vibrational spectra. The anharmonic spectroscopic parameters are calculated using second-order perturbation theory from an anharmonic force field obtained from a nine-dimensional potential energy surface (PES). Finally, we study the formation processes after determining all the minimum energy structures of C_4^-, C_4H, and C_4H^-, and the electron affinities and enthalpy variations. In whole, our theoretical data are compared to the values available from previous theoretical, experimental, and astrophysical works. Generally, an overall agreement is found. Therefore, the predicted unknown data may contribute to the identification and characterization of these important astrophysical molecules.

2. COMPUTATIONAL DETAILS

Electronic structure calculations have been achieved with the MOLPRO program suite (MOLPRO 2002). The search of stationary points and determination of first-order spectroscopic parameters were performed at the coupled cluster including perturbative treatment of triple excitations ((R)CCSD(T); Knowles et al. 1993) and at the complete active space self consistent field (CASSCF; Knowles et al. 2000) levels. For these computations, the Dunning's basis sets including diffuse functions were employed (Dunning 1989; Kendall et al. 1992). The main group of spectroscopic parameters of the $l-C_4H^-$ anion has been calculated with second-order perturbation theory applied on the quadratic, cubic, and quartic force fields derived from a CCSD(T)/aug-cc-pVQZ nine-dimensional PES and the code FIT-ESPEC (Senent 2007). For CASSCF calculations, the active space was defined considering all the π orbitals.

3. DISCUSSION

3.1. The Structure of C_4^-, C_4H, and C_4H^-

Tetracarbon anion, C_4^-, is an important reactant that can be involved in C_4H^- chemical processes. For this reason, it has been treated as starting point for the search of hydrocarbon stationary points and isomers. C_4H^- can also be produced from the neutral C_4H through electron attachment.

In previous papers (Massó et al. 2006; Hochlaf et al. 2007; Inostroza et al. 2008), we performed meticulous theoretical studies on C_4, C_4^+, and C_3Si isomers. C_4 shows two minimum energy structures $l-C_4(X^3\Sigma_g^-)$ and $r-C_4(X^1A_g)$, which are almost isoenergetic. As chains are very sensitive to electronic correlation and the relative energy between isomers is very small, it is very difficult to assert what is its favored geometry. The photoionization of C_4 yields the C_4^+ cation, for which three structures, $l-C_4^+$, $r-C_4^+$, and $d-C_4^+$, are minima on the ground state PES (Hochlaf et al. 2007). As was first observed for the neutral form, the rhombic structure appears to be the most stable at the (R)CCSD(T) level. The substitution of a carbon of C_4 by a silicon atom produces C_3Si, very important astrophysical molecule since it presents a non-zero dipole moment allowing their detection by means of standard spectroscopies. C_3Si possesses at least five minima, two of them are linear, where the most stable forms are cyclic (Inostroza et al. 2008).

We started the present research determining what occurs when C_4 receives one electron. As the relative energy of the neutral C_4 isomers changes sign when single- or multireference methods are employed, the search of structures has been performed using (R)CCSD(T) and CASSCF for comparison. Geometries, energies, and spectroscopic parameters of C_4^- isomers are shown in Table 1. For previous theoretical and experimental studies of C_4^-, see Van Orden & Saykally (1998) and Jochnowitz & Maier (2008).

For C_4^-, three structures, one linear, $l-C_4^-(X^2\Pi_g)$, one rhombic, $r-C_4^-(X^2B_{2g})$ and one of C_{2V} symmetry, $d-C_4^-(X^2B_1)$, represent stable isomers with doublet ground electronic states (see Figure 1). Structures were labeled using the symbols $-l$,$-r$, and $-d$ first employed in our previous studies of carbon chains (Massó et al. 2006; Hochlaf et al. 2007). The linear form is really prominent since the two remaining isomers, $r-C_4^-$ and $d-C_4^-$, lie at least 1.2 eV above in energy. This is in a good agreement with the previous calculations of Watts et al. (1991) who found them above 1.3 eV (30 kcal mol^{-1}). These two secondary min-

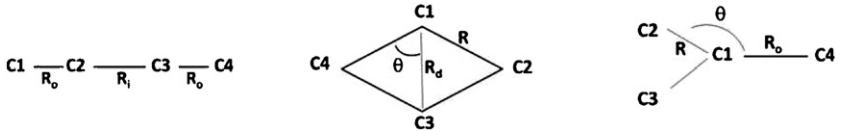

Figure 1. Isomers $l-C_4^-$, $r-C_4^-$, and $d-C_4^-$.

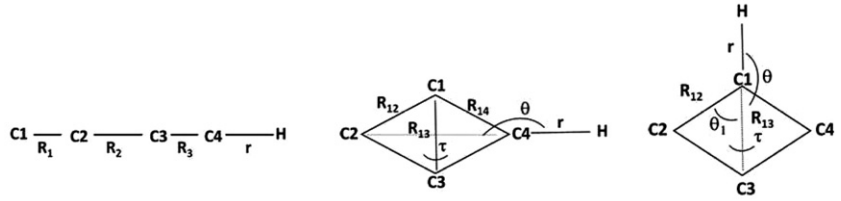

Figure 2. Isomers $l-C_4H$, r^A-C_4H, and r^B-C_4H.

ima are almost isoenergetic, and it is difficult to give a definite assessment about the most stable form of this molecule. Similar to the neutral C_4 cluster (Massó et al. 2006), (R)CCSD(T) and CASSCF calculations provide different order of stabilities for isomers close in energy.

It may be pointed out that $d-C_4^-$ represents a stable form and supports the existence of a third tetracarbon structure as we first predicted (Massó et al. 2006). This is relevant for future astrophysical applications because it shows a non-zero dipole moment (0.9320 D), which permits its detection by radioastronomy. In our previous paper (Massó et al. 2006), we characterized a third structure of C_{2v} symmetry for neutral C_4 although it was not possible to establish if it is a transition state or a low stability isomer because different levels of calculation gave different answers. Furthermore, a $d-C_3Si$ structure, where Si takes the central position, is stable. Obviously, $d-C_4^-$ is stabilized with the electron attachment.

Table 1 lists the (R)CCSD(T)/aug-cc-pVTZ harmonic frequencies of $l-C_4^-$, $r-C_4^-$, and $d-C_4^-$. For the linear form, $l-C_4^-$, we present its harmonic fundamentals computed using CASSCF since (R)CCSD(T) theory fails for the determination of the asymmetric stretching fundamentals of such molecules (we refer to our work on C_4 for further discussions (Senent et al. 2007)). For the symmetric stretching modes, our calculations of 2108 cm^{-1} (ν_1) and 965 cm^{-1} (ν_2) agree with the experimental ones of 2047 $\pm$ 20 cm^{-1} and 936 $\pm$ 20 cm^{-1} deduced from the $C^2\Pi_u \rightarrow X^2\Pi_g$ emission spectra of $l-C_4^-$ trapped in cooled Ne matrices (Schäfer et al. 1996), and previous theoretical calculations of 2082.7 and 911.3 cm^{-1} performed with (R)CCSD(T) (Schmatz & Botschwina 1995). Nevertheless and since the ground electronic state of $l-C_4^-$ is of $^2\Pi$ nature, standard FG algorithm is incompetent to determine the frequencies for the bending modes of such a molecular system because of Renner–Teller effect and spin-orbit coupling. Indeed, the bending motion carries out the break of the electronic state degeneracy. Strictly speaking, one needs to take into account both potential components and all angular (vibrational, electronic, spin-orbit) momenta. This is out of the scope of the present paper since the main aim of these calculations is to provide an overview on the stable forms of C_4^- that might be responsible for the formation of the C_4H^- anion.

The equilibrium rotational constant has been determined to be 4944.9803 MHz, which can be compared with the previous theoretical one of Schmatz and Botschwina ($B_e = 4979.5527$ MHz; Schmatz & Botschwina 1995) and the B_0 measured using two-photon detachment spectroscopy ($B_0 = 4995.4417$ MHz; Zhao et al. 1996). Electron affinity has been calculated to be 3.899 eV

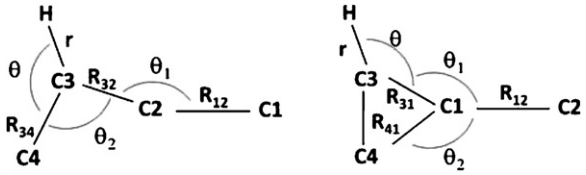

Figure 3. Isomers $p-C_4H^-$ and $d-C_4H$.

that can be compared with the experimental data of 3.882 eV determined by anion photoelectron spectroscopy (Arnold et al. 1991).

The isomers of the hydrocarbons C_4H and C_4H^- determined with (R)CCSD(T) and CASSCF are displayed in Tables 2 and 3 and in Figures 2 and 3. The starting points for the search of stable geometries have been the C_4/C_4^- isomers considering all the possible molecular centers for the hydrogen attachments. For example, starting by *linear*$-C_4$, the H atom can be moved toward to an outer carbon atom or an inner atom producing $l-C_4H$ and $p-C_4H$ (or $l-C_4H^-$ and $p-C_4H^-$). The *rhombic*$-C_4^-$ shows two different active centers situated on the two different diagonals. We called the final structures r^A-C_4H and r^B-C_4H (or $r^A-C_4H^-$ and $r^B-C_4H^-$), respectively. Finally, $d-C_4^-$ shows three active centers, C4, C1, and C2 (or C3), which lead to a C_{2v} transition state (when H is linked to C4), and to $p-C_4H$ and $d-C_4H$ (or $p-C_4H^-$ and $d-C_4H^-$). In total, we found four isomers for C_4H ($l-C_4H$, r^A-C_4H, r^B-C_4H and $d-C_4H$) and four isomers for C_4H^- ($l-C_4H^-$, $r^A-C_4H^-$, $r^B-C_4H^-$, and $p-C_4H^-$).

For both species, the neutral and the anion, the stability of the linear form is prominent, especially for C_4H^- which secondary minima lie above 2 eV. As C_4H is the species first detected (Guélin et al. 1978; Kolbuszewski 1994), it has been treated theoretically in many occasions (Arnold et al. 1991; Dismuke et al. 1975; Kolbuszewski 1994; Woon 1995). It presents two electronic states, $^2\Sigma^+$ and $^2\Pi$ which are near-degenerate. At the (R)CCSD(T)/aug-cc-pVQZ and CASSCF/aug-cc-pVQZ levels of theory, the ground electronic state is the $^2\Sigma^+$, in good agreement with the electron paramagnetic resonance (EPR) spectrum findings (Dismuke et al. 1975). For the energy difference between the Σ and Π states, previous computations predict a small value (2575, Kolbuszewski 1994; 72, Woon 1995; 565, Sobolewski & Adamowicz 1995; 242, CASPT2; and 283, MRCI, Graf et al. 2001—all values are in cm^{-1}) and the slow electron velocity-map imaging spectroscopy provides a value of 213 cm^{-1} (Zhou et al. 2007). Present calculations confirm this short gap between these two low lying states.

Table 2
Electronic Energies (in Hartrees, E), Relative Energies (in eV, E_r), and Structural Parameters (distances in Å; angles in degrees) of C_4H Isomers

Isomers		(R)CCSD(T)	CASSCF	RCCSD(T)[a]
		aug-cc-pVQZ	aug-cc-pVQZ	Spectroscopic Parameters
$l-C_4H$	$X^2\Sigma^+$	$R_1 = 1.2164$	$R_1 = 1.2108$	$B_e = 4727.6009$
($C_{\infty v}$)		$R_2 = 1.3765$	$R_2 = 1.3785$	$\mu = 0.8924$
		$R_3 = 1.2118$	$R_3 = 1.2157$	
		$r = 1.0635$	$r = 1.0537$	
		$E = -152.517963$	$E = -152.072306$	
	$^2\Pi$	$R_1 = 1.2947$	$R_1 = 1.2849$	$B_e = 4631.4765$
		$R_2 = 1.3420$	$R_2 = 1.3445$	$\mu = 4.3336$
		$R_3 = 1.2264$	$R_3 = 1.2166$	
		$r = 1.0649$	$r = 1.0691$	
		$E = -152.517922$	$E = -152.059408$	
r^A-C_4H	X^2A'	$R_{13} = 1.5295$	$R_{13} = 1.5407$	$A_e = 36004.3879$, $B_e = 12658.7262$
(C_s)		$R_{14} = 1.3998$	$R_{14} = 1.4078$	$C_e = 9365.8309$, $\mu = 4.0523$
		$R_{12} = 1.4555$	$R_{12} = 1.4568$	3341(a'), 1444(a''), 1253(a')1004(a'')
		$r = 1.0707$	$r = 1.0691$	927(a'), 751(a''), 465(a'')
		$\theta = 180.0$, $\tau = 180.1$	$\theta = 158.4$, $\tau = 176.4$	442(a''), 80(a')
		$E = -152.481771$	$E = -152.025956$	
		$E_r = 0.98$	$E_r = 1.27$	
r^B-C_4H	X^2A''	$R_{12} = 1.4085$	$R_{12} = 1.4823$	$A_e = 21814.907$, $B_e = 16196.458$
(C_s)		$R_{13} = 2.0255$	$R_{13} = 2.0406$	$C_e = 10426.979$, $\mu = 3.1959$
		$r = 1.0778$	$r = 1.0669$	3259(a'), 1358(a'), 1181(a'), 1159(a'')
		$\theta_1 = 43.4$	$\theta_1 = 43$	949(a''), 862(a'), 666(a')
		$\theta = 147$, $\tau = 128.3$	$\theta = 155.3$, $\tau = 150.6$	623(a''), 511(a')
		$E = -152.458062$	$E = -152.000203$	
		$E_r = 1.63$	$E_r = 1.96$	
$d-C_4H$	X^2A''	$R_{12} = 1.3242$	$R_{12} = 1.3261$	$A_e = 37277.0291$, $B_e = 8654.94$
(C_s)		$R_{13} = 1.4131$	$R_{13} = 1.3980$	$C_e = 7023.9316$, $\mu = 3.3652$
		$R_{14} = 1.5197$	$R_{14} = 1.5894$	3258(a'), 1678(a'), 1380(a'), 976(a')
		$r = 1.0758$	$r = 1.0645$	914(a'), 751(a''), 675(a')
		$\theta_1 = 146.5$, $\theta_2 = 159.2$	$\theta_1 = 165.2$, $\theta_2 = 141.3$	346(a''), 166(a')
		$\theta = 136.1$	$\theta = 136.6$	
		$E = -152.446374$	$E = -152.026859$	
		$E_r = 1.95$	$E_r = 1.24$	

Notes. Equilibrium rotational constants (in MHz), harmonic frequencies (in cm^{-1}), and dipole moment (in Debyes).
[a] $l-C_4^-$ frequencies and all the dipole moments were calculated at the CASSCF/aug-cc-pVTZ level. Dipole moment origins are the centers of mass.

Indeed, a 9 cm^{-1} gap is calculated with (R)CCSD(T) and 2831 cm^{-1} with CASSCF.

The spectroscopic parameters for the ground electronic state of $l-C_4H$ are shown in Table 2, where the harmonic wavenumbers are missing since the calculations with the standard algorithms implemented in MOLPRO do not provide realistic values given the proximity of the degenerate $^2\Pi$ state. Renner–Teller effect and spin-orbit interaction and non-adiabatic couplings disturb the pattern of its rovibronic structure. Experimental frequencies are given in Shen et al. (1990). As was expected, electron attachment produces a very slight deformation. The (R)CCSD(T)/aug-cc-pVQZ rotational constants of $l-C_4H$ and $l-C_4H^-$ are $B_e = 4727.6009$ MHz and $B_e = 4625.6546$ MHz, respectively. For the anion, our value compare quite well with experimental determinations, i.e., $B_0 = 4758.48$ MHz (Botschwina & Oswald 2008) and $B_0 = 4654.9449$ MHz (Gupta et al. 2007). The dipole moment of $l-C_4H^-$ has been determined to be 6.8368 D (origin = center of mass), which is slightly larger than the experimentally measured value of 6.2 D (Agúndez et al. 2008).

For the remaining isomers, the first doublet excited electronic state lies relatively far to the ground state. In contrast to the linear forms, differences of energy are larger than 1 eV allowing the determination of band positions with standard methods. For both charged and neutral species, there are two rhombic forms A and B products of hydrogen capture in different actives sites. In the A forms, the cyclic structure of C_4^- is preserved during the hydrogen capture, whereas, in the B forms, the molecular cycle is not planar but shows two diagonals almost identical. r^A-C_4H represents the most stable non-linear isomer lying at 0.98 eV over $l-C_4H$. For the anion, both rhombic forms present similar stabilities (2.64 eV and 2.04 eV with respect to $l-C_4H$). For these species, Table 2 lists the first-order spectroscopic parameters, the (R)CCSD(T)/aug-cc-pVQZ rotational constants, (R)CCSD(T)/aug-cc-pVTZ harmonic wavenumbers, and CASSCF/aug-cc-pVTZ dipole moments.

Finally, Tables 4 and 5 show the adiabatic electronic affinities (EA) and the enthalpy differences ΔH calculated with (R)CCSD(T)/aug-cc-pVQZ for all isomers. For the determination of H, the counterpoise correction (Boys & Bernardi 1970) for the basis set superposition error has been considered. We have also taken into account the zero-point vibrational energy (ZPE) at the harmonic level. For the linear form, the calculated EA of 3.56 eV is in a good agreement with the experimental value of 3.558 ± 0015 eV determined using photoelectron spectroscopy (Taylor et al. 1998).

Table 3
Electronic Energies (in Hartrees, E), Relative Energies (in eV, E_r), and Structural Parameters (distances in Å; angles in degrees) of C_4H^- Isomers

Isomers		(R)CCSD(T)	CASSCF	RCCSD(T)[a]
		aug-cc-pVQZ	aug-cc-pVQZ	Spectroscopic Parameters
$l-C_4H^-$	$X^1\Sigma^+$	$R_1 = 1.2573$	$R_1 = 1.2467$	$B_e = 4625.6546$
($C_{\infty v}$)		$R_2 = 1.3720$	$R_2 = 1.3744$	$\mu = 6.8368$
		$R_3 = 1.2261$	$R_3 = 1.2265$	3456(σ), 2108(σ), 1913(σ), 875(σ)
		$r = 1.0615$	$r = 1.0515$	498(π), 386(π), 209(π)
		$E = -152.651730$	$E = -152.166016$	
$r^A-C_4H^-$	X^1A'	$R_{13} = 1.4749$	$R_{13} = 1.4892$	$A_e = 36370.3486$, $B_e = 12090.2957$
(C_s)		$R_{14} = 1.4882$	$R_{14} = 1.5010$	$C_e = 9357.2020$, $\mu = 1.9156$
		$R_{12} = 1.4233$	$R_{12} = 1.4216$	2980(a'), 1418(a'), 1220(a'), 1033(a'')
		$r = 1.0979$	$r = 1.0857$	1010(a'), 877(a'), 581(a'')
		$\theta = 115.6$, $\tau = 173.6$	$\theta = 115.4$, $\tau = 174.5$	526(a'), 229(a'')
		$E = -152.554862$	$E = -152.055137$	
		$E_r = 2.64$	$E_r = 3.02$	
$r^B-C_4H^-$	X^1A'	$R_{12} = 1.4716$	$R_{12} = 1.4790$	$A_e = 19643.9165$, $B_e = 17008.1341$
(C_s)		$R_{13} = 1.7610$	$R_{13} = 1.7723$	$C_e = 10829.5264$, $\mu = 3.2335$
		$r = 1.0867$	$r = 1.0752$	3108(a'), 1283(a'), 1269(a''), 1090(a')
		$\theta_1 = 51.9$	$\theta_1 = 52$	1000(a''), 835(a'), 658(a')
		$\theta = 133.8$, $\tau = 125$	$\theta = 134$, $\tau = 126.2$	585(a'), 354(a'')
		$E = -152.543699$	$E = -152.058031$	
		$E_r = 2.94$	$E_r = 2.93$	
$d-C_4H^-$	X^1A'	$R_{12} = 1.2677$	$R_{12} = 1.2524$	$A_e = 38781.0190$, $B_e = 7807.6104$
(C_s)		$R_{23} = 1.4540$	$R_{23} = 1.4254$	$C_e = 6499.1628$, $\mu = 5.9568$
		$R_{34} = 1.3111$	$R_{34} = 1.3153$	3220(a'), 1883(a'), 1563(a'), 1025(a')
		$r = 1.0780$	$r = 1.0906$	878(a'), 636(a''), 341(a'')
		$\theta_1 = 174$, $\theta_2 = 81.3$	$\theta_1 = 177.8$, $\theta_2 = 130.9$	261(a'), 146(a')
		$\theta = 147$	$\theta = 108.3$	
		$E = -152.573340$	$E = -152.074295$	
		$E_r = 2.13$	$E_r = 1.74$	

Notes. Equilibrium rotational constants (in MHz), harmonic frequencies (in cm^{-1}), and dipole moment (in Debyes).
[a] $l-C_4^-$ frequencies and all the dipole moments were calculated at the CASSCF/aug-cc-pVTZ level. Dipole moment origins are the centers of mass.

Table 4
(R)CCSD(T)/aug-cc-pVQZ Adiabatic Electron Affinities (in eV, EA) of C_4H

Processes	EA	Exp.	Ref.
$l-C_4H + e^- \rightarrow l-C_4H^-$	3.56	3.558 ± 0015	Taylor et al. (1998)
$r^A-C_4H + e^- \rightarrow r^A-C_4H^-$	1.98		
$r^B-C_4H + e^- \rightarrow r^B-C_4H^-$	2.35		
$d-C_4H + e^- \rightarrow p-C_4H^-$	3.47		

(This table is available in its entirety in a machine-readable form in the online journal. A portion is shown here for guidance regarding its form and content.)

Table 5
(R)CCSD(T)/aug-cc-pVQZ Formation Energies (in eV, ΔH) of C_4H and C_4H^-

Processes	ΔH
$l-C_4^- + H \rightarrow l-C_4H + e^-$	−1.00
$r-C_4^- + H \rightarrow r^A-C_4H + e^-$	−1.30
$r-C_4^- + H \rightarrow r^B-C_4H + e^-$	−0.60
$d-C_4^- + H \rightarrow d-C_4H + e^-$	−0.26
$l-C_4^- + H \rightarrow l-C_4H^-$	−4.57
$l-C_4^- + H \rightarrow p-C_4H^-$	−2.48
$r-C_4^- + H \rightarrow r^A-C_4H^-$	−3.27
$r-C_4^- + H \rightarrow r^B-C_4H^-$	−2.96
$d-C_4^- + H \rightarrow p-C_4H^-$	−3.73

Table 6
(R)CCSD(T)/aug-cc-pVTZ Quadratic F_{ij} Force Field of $l-C_4H^-$

i	j	F_{ij}	i	j	F_{ij}	l	j	F_{ij}
1	1	6.4194	2	1	−0.0898	6	5	0.1139
2	2	14.4599	3	1	−0.0085	7	5	0.0155
3	3	12.0322	3	2	−0.3703	7	6	−0.0069
4	4	7.1438	4	1	−0.0047			
5	5	0.4926	4	2	0.8306			
6	6	0.1175	4	3	0.3307			
7	7	0.1953						

Note. The cubic and quartic force fields are provided as supplementary material.

3.2. Spectroscopic Characterization of the Ground Electronic State of $l-C_4H^-$

Our electronic calculations reveal that the electronic ground state of $l-C_4H^-$ anion is the $X^1\Sigma^+$. Presently, we compute the spectroscopic parameters of $l-C_4H^-$ ($X^1\Sigma^+$) using second-order perturbation theory after producing a CCSD(T)/aug-cc-pVQZ anharmonic force field, computed from the determination of a local full-dimensional PES defined as functions of the internal coordinates. We follow the same procedure described already (Senent et al. 2007; Massó et al. 2007). Briefly, a grid of 2156 geometries around the CCSD(T) reference structure (cf. Table 1) was selected taking in consideration symmetry and energy criteria. In total, the stretching coordinates vary up

Table 7
Anharmonic Spectroscopic Parameters of Various $l-C_4H^-$ Isotopomers Calculated from the (R)CCSD(T)/aug-cc-pVQZ Force Field Using Second-order Perturbation Theory[a]

Spectroscopic Parameters	CCCCH$^-$ (b)	CCCCD$^-$ (c)	^{13}CCCCH$^-$	C^{13}CCCH$^-$	CC^{13}CCH$^-$	CCC^{13}CH$^-$
$\omega_1(\sigma)$	3463	2652	3447	3462	3463	3463
$\omega_2(\sigma)$	2113	2061	2100	2076	2095	2108
$\omega_3(\sigma)$	1923	1870	1911	1910	1892	1901
$\omega_4(\sigma)$	881	867	870	876	877	867
$\omega_5(\pi)$	512	491	512	504	506	511
$\omega_6(\pi)$	419	337	415	416	419	419
$\omega_7(\pi)$	215	207	214	214	211	212
$\nu_1(\sigma)$	3312	2560	3298	3311	3312	3312
$\nu_2(\sigma)$	2066	2020	2055	2031	2049	2060
$\nu_3(\sigma)$	1885	1835	1872	1872	1855	1863
$\nu_4(\sigma)$	875	850	863	870	871	868
$\Delta\nu_4$	1.6	0.01	1.39	1.13	1.76	2.15
$\nu_5(\pi)$	506	482	506	497	501	506
$\nu_6(\pi)$	402	326	213	399	402	402
$\nu_7(\pi)$	214	206	398	213	211	211
$2\nu_1$	6513	5069	6485	6512	6513	6513
$2\nu_2$	4119	4026	4095	4049	4085	4108
$2\nu_3$	3756	3662	3733	3732	3695	3713
$2\nu_4$	1740	1695	1718	1731	1733	1726
$2\nu_5$	1010	962	1011	993	999	1011
$2\nu_6$	806	655	799	799	805	806
$\Delta\nu_6$	−3.6	−0.1	−3.4	−3.7	−3.9	−3.9
$2\nu_7$	428	411	426	422	421	423
$\alpha_1 x10^{-3}$	7.551	11.214	6.933	7.43	7.525	7.161
$\alpha_2 x10^{-3}$	24.137	22.117	24.052	24.122	22.751	22.951
$\alpha_3 x10^{-3}$	16.159	12.648	15.227	15.196	16.394	16.091
$\alpha_4 x10^{-3}$	10.786	9.432	10.216	10.825	10.804	10.147
$\alpha_5 x10^{-3}$	−7.024	−7.221	−6.772	−6.718	−6.782	−6.758
$\alpha_6 x10^{-3}$	−5.907	−7.999	−5.356	−5.975	−5.952	−5.631
$\alpha_7 x10^{-3}$	−15.166	−13.311	−14.643	−14.959	−14.642	−14.748
B_e	4625.8098	4295.2771	4486.3384	4609.2198	4603.1567	4465.5761
B_0	4624.5907	4296.103	4484.8955	4608.0855	4601.7961	4464.5377
B_{ν_1}	4617.0397	4284.8885	4477.9628	4600.6554	4594.2710	4457.3767
B_{ν_2}	4600.4535	4273.9860	4460.8437	4583.9633	4579.0456	4441.5866
B_{ν_3}	4608.4339	4283.4548	4469.6681	4592.8891	4585.4024	4448.4472
B_{ν_4}	4613.8048	4386.6711	4474.6792	4597.2607	4590.9922	4454.3907
B_{ν_5}	4631.6143	4303.3240	4491.6678	4614.8036	4608.5779	4471.2955
B_{ν_6}	4630.4974	4304.1013	4490.2509	4614.0608	4607.7481	4470.1684
B_{ν_7}	4639.7564	4309.4138	4499.5386	4623.0445	4616.4385	4479.2857
$D_e x10^{-3}$	0.54399	0.45047	0.51038	0.5426	0.5408	0.50622
$H_e x10^{-10}$	−0.13998	−0.0915	−0.11822	−0.14869	−0.14768	−0.11877
q_5	−3.6491	−3.2960	−3.4326	−3.6608	−3.6472	−3.4044
q_6	−6.9811	−6.2448	−6.5985	−6.9670	−7.0214	−6.5835
q_7	−3.6784	−3.9106	−3.4960	−3.7016	−3.6537	−3.4286

Notes.
[a] Previous anharmonic calculations performed with CCSD(T)/avzq+ (Botschwina & Oswald 2008).
[b] Previous experimental values for CCCCH: $\nu_6 = 430\pm5$ cm^{-1} and $\nu_7 = 219\pm5$ cm^{-1} (Pino et al. 2002); $B_0 = 4654.9449$ MHz, D=0.5875 x10^{-3}MHz (Gupta et al. 2007); $B_0 = 4654.94502$ MHz, D=0.58771 x10^{-3}MHz and H=0.93 x10^{-10} (Amano 2008).
[c] Previous experimental values for CCCCD: $\nu_6 = 396\pm5$ cm^{-1} and $\nu_7 = 212\pm5$ cm^{-1}(Pino et al. 2002).

to 0.15 Å and the in-plane angles, which follow the definition of Hoy et al. (1972), up to 36°. The analytic expression of the PES, that contains four degree coupling terms, is a well-known product of Taylor series:

$$V(q_1, q_2, \cdots q_n) = \sum_{i=1}^{n}\sum_{j=1}^{n}\frac{1}{2}f_{ij}q_iq_j + \sum_{i=1}^{n}\sum_{i=1}^{n}\sum_{k=1}^{n}\frac{1}{6}f_{ijk}q_iq_jq_k + \sum_{i=1}^{n}\sum_{j=1}^{n}\sum_{k=1}^{n}\sum_{l=1}^{n}\frac{1}{24}f_{ijkl}q_iq_jq_kq_l, \quad (1)$$

where $q_m = S_m - S_m^{REF}$ represents the displacements of the corresponding internal coordinate. The standard deviation of the linear fit was 7 cm^{-1} ($R^2 = 1.0$).

Table 6 presents the most significant terms of the anharmonic quartic force field, and Table 7 the anharmonic spectroscopic parameters of six isotopomers calculated with the FIT-ESPEC code (Senent 2007). The full force field terms are supplied as supplementary material. The harmonic wavenumbers, fundamental stretching bands and the alpha and *l-doubling* constants of Table 7 may be compared with previous calcula-

tions (Botschwina & Oswald 2008). The band positions corresponding to the large amplitude modes and some rotational parameters may be compared with the few available experimental data (Pino et al. 2002; Gupta et al. 2007; Amano 2008). To our knowledge, there is no available data for the remaining four isotopomers containing ^{13}C. We provide the most relevant spectroscopic parameters for a linear molecule (band centers, rotational constants, vibration–rotation terms (α), and *l-doubling* parameters). Especially, our calculations show that a Fermi resonance displaces the fundamental ν_4 and the $2\nu_6$ overtone by an amount of 1–2 and 3–4 cm^{-1}, respectively.

In Table 7, band centers for C_4H^- and C_4D^- are compared with the CCSD(T) calculations of Botschwina & Oswald (2008). These authors deduced their vibrational spectra with a four-dimensional anharmonic model that does not contemplate the bending modes and the stretching–bending interaction. Our calculations show that these effects are not that large. Therefore, a reasonable agreement is found with Botschwina and Oswald results, although we use a full nine-dimensional model.

4. CONCLUSIONS

Using ab initio methodologies, we characterized the stable forms of the astrophysically important C_4^-, C_4H, and C_4H^-. In the present contribution, several branched and cyclic isomers are found in addition to the already known linear structures. Most of these isomers are predicted for the first time. We also provide an accurate set of spectroscopic parameters for the most stable isomers. These data are useful for the identification of these species in laboratory and in astrophysical media. Moreover, we examined the thermochemistry of the hydrogen attachment and the electron attachment reactions that may lead to the formation of the C_4H^- from either C_4^- or C_4H. Generally, a good agreement is found with the available experimental determinations. In the near future, we plan to investigate the lowest electronic excited states of the C_4H^- anion and the mechanisms of its formation through ion–molecule reactions between H^- and C_4 or H and C_4^-.

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